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Tagging multiphoton ionization events by two-dimensional photoelectron spectroscopy

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Two-dimensional photoelectron spectroscopy has been used to supply process-specific labels to multiphoton ionization events. Employing these tags, the authors can construct excitation and photoelectron spectra along predefined excitation routes in the neutral manifold and ionization routes to the ionic manifold from one single two-dimensional photoelectron spectrum. These results offer a novel way to elucidate the vibronic and dynamic properties of excited and ionic states. © 2007 American Institute of Physics. [DOI: [10.1063/1.2738465](https://doi.org/10.1063/1.2738465)]

I. INTRODUCTION

Multiphoton ionization–photoelectron spectroscopy (MPI-PES) is a powerful tool to accurately determine energies of excited states and ionization potentials, as well as to probe excited state properties. A MPI-PES experiment is traditionally performed in two steps. In the first step, an excitation spectrum is recorded by scanning the wavelength of a laser focused into a gaseous sample and measuring the total yield of photoelectrons. If the laser flux is so high that non-resonant n -photon absorption leads to appreciable ionization, one generally observes a step in the ionization yield when the excitation frequency is scanned over the n -photon ionization threshold. From this step the ionization potential of the molecule can be determined directly. On the other hand, if at the n' -photon level resonance occurs with an excited vibronic state and the molecule is ionized in a sequential $n' + m$ absorption process, the ionization probability is enhanced and the photoelectron yield increases. Peaks in the excitation spectrum thus correspond to resonances with excited vibronic states of the neutral molecules. In the second step, the laser is tuned to a specific vibronic resonance in the excitation spectrum and the distribution of photoelectron kinetic energies is determined, resulting in a photoelectron spectrum that can be considered as a fingerprint of the excited state.

Unfortunately, more often than not the situation is not so straightforward. It is not always clear what process is associated with a particular multiphoton ionization event: How many photons are involved in the excitation and ionization steps (in the case of resonance enhanced ionization)? Is it the

molecule that is ionized or a fragment? To what extent do superexcited states above the ionization threshold play a role? etc. Often, one is able to resolve these issues in due course by very careful and fastidious experimentation, for example, by using various excitation wavelengths, precise calibration, multicolor ionization schemes, and photoelectron-photoion coincidence measurements.¹ However, this requires a lot of time and experimental effort. In this paper, we present two-dimensional photoelectron spectroscopy (2D-PES) as a fast, simple, and efficient tool that enables direct visual recognition of the processes responsible for multiphoton ionization events. We show that the wealth of information contained in these 2D spectra can be analyzed in a straightforward way to efficiently map out the vibrational manifolds of both excited neutral and ionic states. Previously, 2D-PES combined with *one-photon* ionization has been applied with great success for the study of above-threshold processes such as autoionization and postcollision interactions.^{1,2} We will demonstrate that the comprehensive nature of 2D-PES is *particularly* valuable in *multiphoton* ionization experiments.

II. EXPERIMENTAL DETAILS

The experimental setup used has been described in detail elsewhere.^{3,4} Briefly, the light from an excimer pumped dye laser is focused into the ionization chamber of a magnetic bottle spectrometer⁵ by a quartz lens with a focal length of 175 mm. Samples are introduced into the ionization region of the spectrometer as an effusive beam. The photoelectrons formed in the ionization region are parallelized by a strongly diverging magnetic field, and they enter a 0.5 m flight tube where a homogeneous magnetic field guides them to a pair of stacked microchannel plates (MCPs). It is often useful to

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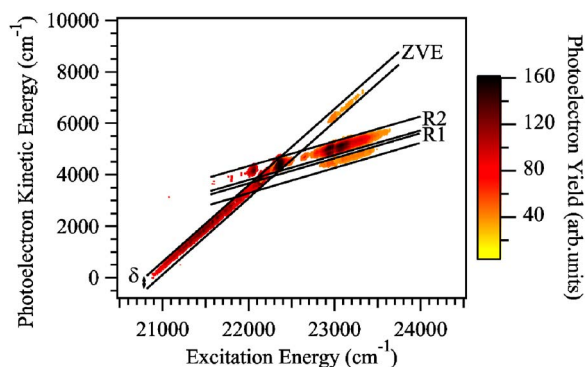


FIG. 1. (Color online) Contour plot of the three-photon 2D-PE spectrum of indole.

use a small electric field to push slow photoelectrons toward the flight tube. For this purpose, two copper electrodes are mounted in the ionization region. The ac signal of the MCPs is recorded and averaged by a 500 MHz digital oscilloscope that is read out by a personal computer for further analysis.

III. RESULTS AND DISCUSSION

The essence of 2D-PES is simple. In the conventional two-step process described in I, dispersed photoelectron spectra are recorded in a separate experiment for selected peaks in the excitation spectrum. In 2D-PES, instead, we record the entire dispersed photoelectron spectrum at all steps of a continuous excitation wavelength scan, and plot the results, as shown in Fig. 1. The major advantage of this approach is that signals are now not only characterized by excitation and photoelectron energies but also by a *slope*. This slope is effectively a label that tells us what process is responsible for the signal.

In order to quickly and efficiently record the photoelectron spectrum at all steps of the excitation scan, the time-of-flight spectra recorded on the oscilloscope are directly converted to a linear energy scale by application of the following formula:

$$E = \frac{1}{2} m_e l^2 \frac{l}{t - t_0} \frac{1}{e}, \quad (1)$$

where E is the photoelectron energy in eV, m_e the mass of the electron, l the distance from the ionization region to the detector, t the flight time, t_0 the moment of ionization, and e the elementary charge. In practice t_0 and l are fitted to a known spectrum (typically that of xenon). The disadvantage of retrieving photoelectron spectra in this way is that, because of the limited time resolution of the measurement, the resolution is lower for faster photoelectrons. When recording a standard one-dimensional PES, we use a scanning retardation voltage and convert only the high resolution part of the time-of-flight spectrum. In this way, a uniform (high) resolution can be obtained.³ By using a direct conversion of the time-of-flight spectrum and sacrificing resolution, we, however, gain in 2D-PES access to the full photoelectron spectrum at every excitation wavelength.

In the following, we will demonstrate the effectiveness of 2D-PES by its application to the indole molecule. From a

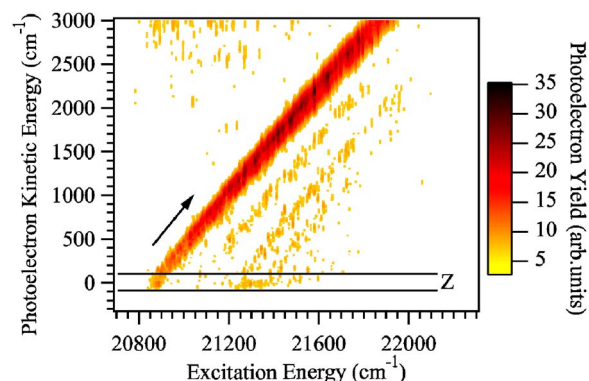


FIG. 2. (Color online) Zoom-in of the three-photon 2D-PE spectrum of indole showing ionization to various vibrational levels of the ion.

single 2D-PE spectrum we will determine straightaway (i) the ionization potential (IP), (ii) the vibronic structure of the cation, (iii) the term values of two Rydberg states, and (iv) their vibrational structure. For the simultaneous determination of these particular properties, a one-color three-photon MPI scheme is well suited, and is therefore applied here. In general, however, the 2D-PES technique can be used with any $(n+m)$ one- or multicolor MPI scheme, the choice for a particular scheme depending only on the process(es) one would like to study.

Figure 1 shows the three-photon 2D-PE spectrum for an effusive beam of indole for excitation energies from 20 500 cm^{-1} , just below the three-photon ionization threshold, to 24 500 cm^{-1} . At the three-photon threshold of about 20 860 cm^{-1} , photoelectrons with zero kinetic energy are detected. As the excitation energy is increased, so is the kinetic energy of the photoelectrons (PKE). In the 2D-PE spectrum this leads to what we will call a *ridge* with a characteristic slope of $\Delta\text{PKE}/\Delta h\nu$. Obviously, for the ridge resulting from three-photon ionization to the vibrational ground state of the ion the slope is 3. Since it is associated with ions with zero vibrational energy, the ridge is marked in Fig. 1 as ZVE. We define the ZVE spectrum as the integral $f_{\text{ZVE}}(x) = \int_{3(x-x_0)-(1/2)\delta}^{3(x-x_0)-(1/2)\delta} S(x,y) dy$, where $S(x,y)$ is the photoelectron yield, x_0 is the x coordinate at the onset of the ridge, and δ is the width defined by the lines indicated in Fig. 1. This ZVE spectrum, displayed in Fig. 3(a), contains the three-photon ionization threshold corresponding to an IP of 7.760 ± 0.005 eV, a value that is in excellent agreement with the most accurate literature value of 7.7602 ± 0.0006 eV.⁶ The other features present in the ZVE spectrum will be discussed below.

Apart from the energy of the vibrational ground state level of the ion, the 2D-PE spectrum also provides information on vibrationally excited levels of the ion. Figure 2 is a zoom in of the low-energy part of the 2D-PE spectrum of Fig. 1. At various energies above the three-photon threshold, ridges with a slope of 3 can be observed. These ridges are associated with nonresonant three-photon ionization to vibrationally excited states of the ion. The most direct way to extract a vibrational spectrum of the ion is to integrate the signal of the photoelectrons with near-zero energy between the lines marked by “Z” in Fig. 2, a procedure that, in fact,

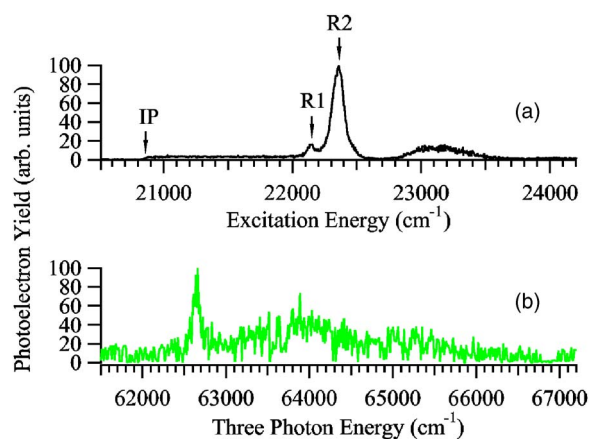


FIG. 3. (Color online) (a) Zero vibrational energy spectrum of indole showing the ionization potential (IP) and the 0_0^0 transitions to two Rydberg states (R_1 and R_2). (b) ZEKE spectrum of indole.

closely corresponds to the way zero electron kinetic energy (ZEKE) spectroscopy was set up originally.^{7–10} In the present case, however, this leads to a spectrum with a rather poor signal-to-noise ratio [Fig. 3(b)], because only a fraction of the information available in the 2D-PE spectrum is exploited. A far better way to obtain what we will call the *projected* ZEKE (PZ) spectrum is to integrate the ridges over a much larger photoelectron energy range, 2500 cm⁻¹ in the present case, in the direction marked by the arrow in Fig. 2. This projected spectrum is defined by the integral $f_{PZ}(x) = \int_0^{2500} S(x + 1/3y, y) dy$ and is displayed in Fig. 4(a).

Within the Condon approximation and assuming that the electronic transition moment is independent of the photoelectron kinetic energy, the intensities in the PZ spectrum are directly proportional to the Franck-Condon factors between the vibrational wave function of the electronic ground state of the neutral and that of the ion. Figure 4(d) displays such a Franck-Condon simulation based on the equilibrium geometries and associated force fields calculated with density functional theory, using the B3LYP exchange correlation functional^{11–13} and a triple- ζ basis set augmented with polarization functions (def-TZVP).¹⁴ Comparison of this model with the experimental spectrum of Fig. 4(a) results in a very satisfying agreement.

The ZVE spectrum in Fig. 3(a) displays resonances at 22 144, 22 360, and 23 130 cm⁻¹ that, in principle, could occur at either the one- or the two-photon level. It is well known that the adiabatic transition energy of the lowest excited state of indole in the gas phase is 35 233 cm⁻¹.¹⁵ We can therefore safely assume that the resonance occurs at the two-photon level. However, even without any prior knowledge of the excited states, the labels of the ridges provided by the slope in the 2D-PE spectrum of Fig. 1 allow us to draw the exact same conclusion. At the resonances at 22 144 and 22 360 cm⁻¹ the ridge with a slope of 3 branches off into ridges with a slope of 1 (marked as R_1 and R_2). For these latter ridges only one-third of the three-photon energy ends up as kinetic energy of the photoelectron, the rest remains in the ion as vibrational energy. This behavior strongly suggests a 2+1 ionization process via two-photon resonant states at 44 288 and 44 720 cm⁻¹ with geometrical and vibrational

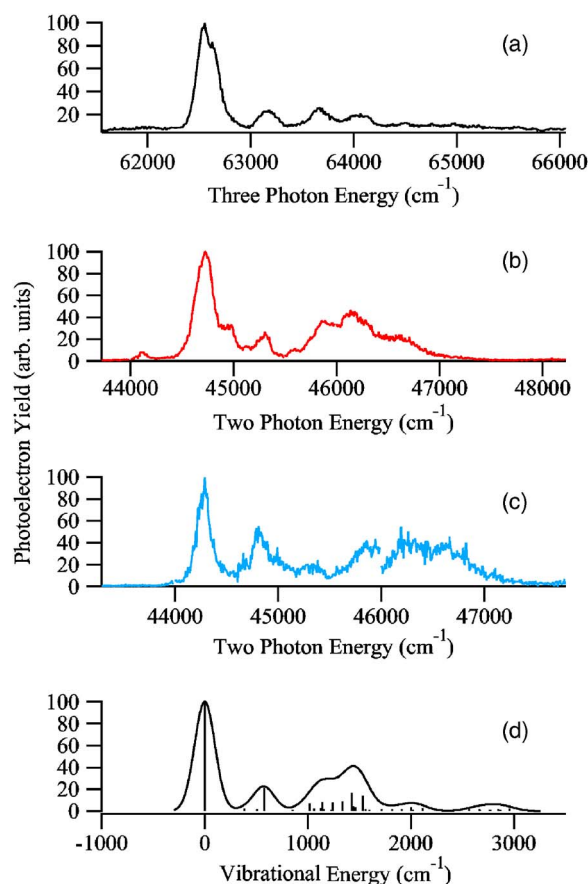


FIG. 4. (Color online) (a) Projected ZEKE spectrum of indole. (b) Vibronic excitation spectrum of R_2 . (c) Vibronic excitation spectrum of R_1 . (d) Franck-Condon simulation of $D_0 \leftarrow S_0$ ionization. The spectrum has been constructed by convolution of the indicated stick spectrum with a Gaussian function with a full width at half maximum of 230 cm⁻¹.

properties very similar to those of the ion. Based on their quantum defect of 0.55 and 0.52, respectively, we therefore assign the resonant states to members of the $3p$ Rydberg manifold. Such an assignment is completely in line with the results of CASPT2 calculations¹⁶ that predicted vertical excitation energies of 43 230 and 43 310 cm⁻¹ for the $3p_x$ and $3p_y$ states. The $3p_z$ state was calculated at a lower energy (42 020 cm⁻¹) and is therefore a less likely candidate.

The third resonant feature in the ZVE spectrum—the broad band centered around a one-photon energy of 23 130 cm⁻¹—is harder to explain. One might be tempted to assign it to—in that case lifetime-broadened—the $3p_z$ Rydberg state, but such an assignment would imply that the CASPT2 calculations predicted an incorrect ordering of the $3p$ manifold, and would be inconsistent with the lack of branching into a ridge with a slope of 1 at 23 130 cm⁻¹. The latter observation also argues against nondiagonal ionization from the R_2 Rydberg state as a possible explanation for the appearance of the 23 130 cm⁻¹ feature.

Vibronic spectra of the two $3p$ Rydberg states can be extracted from the 2D-PE spectrum by integration over the R_1 and R_2 ridges using the integrals $f_{R_i}(x) = \int_{(x-x_{R_i})+y_{R_i}-(1/2)\delta}^{(x-x_{R_i})+y_{R_i}+(1/2)\delta} S(x, y) dy$, with x_{R_i} and y_{R_i} the x and y coordinates of the maximum of the ridge R_i in the 2D-PE spectrum. The spectra, shown in Figs. 4(b) and 4(c), closely re-

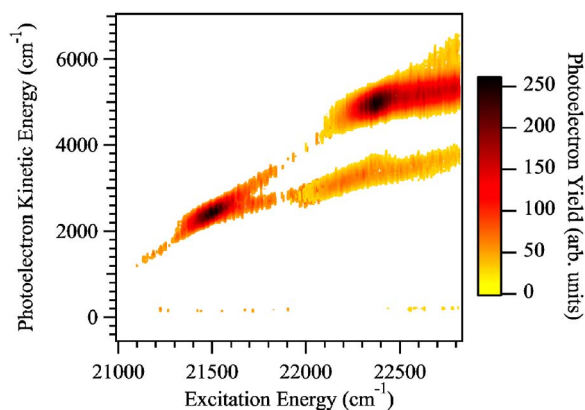


FIG. 5. (Color online) Contour plot of the three-photon 2D-PE spectrum of 5-fluoro-3-methylindole.

semble the spectrum obtained for nonresonant three-photon ionization [Fig. 4(a)] and its simulation [Fig. 4(d)]. This provides further confirmation of the assignment of the resonant states as Rydberg states. Redshifted from the origin band in Fig. 4(b), a small peak is visible. We assign this peak to a hot band, i.e., a transition from a thermally excited vibrational level in the ground state to the vibrationless Rydberg state.

The applicability of 2D-PES is further illustrated in Fig. 5, which shows the three-photon 2D-PE spectrum of 5-fluoro-3-methyl indole.¹⁷ An obvious difference with the experiments on indole is that here the laser is not scanned over the actual three-photon threshold. Nevertheless, the IP can readily be determined from an extrapolation of the ridge with a slope of 3 to zero photoelectron kinetic energy, and is determined as 7.70 ± 0.01 eV.¹⁸ The 2D-PE spectrum gives evidence for two close-lying Rydberg states at 43 000 and 44 740 cm^{-1} . Based on their quantum defects of 0.61 and 0.49, respectively, and the analogy with indole, we assign these two states to the $3p_x$ and $3p_y$ Rydberg states.

IV. SUMMARY AND CONCLUSIONS

We have shown that two-dimensional photoelectron spectroscopy offers unique possibilities to tag multiphoton ionization events. The labels provided by the technique enable one to read off directly from the 2D-PE spectrum the photophysical process responsible for the appearance of a particular subset of photoelectrons. As a result, various types

of excitation spectra of intermediate, resonance enhancing, neutral states and of ionic states, as well as photoelectron spectra can be extracted unambiguously from a single 2D-PE spectrum. In the present study, we have successfully employed the technique to disentangle various multiphoton ionization pathways and to determine the excitation energies of the $3p_x$ and $3p_y$ Rydberg states of indole and 5-fluoro-3-methyl indole. In a forthcoming paper, we will show the significant advantages the technique offers to elucidate the singlet-triplet coupling between the lower-lying excited states of acetylene.

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